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Cl_2-O_2 LEACHING OF MASSIVE SULFIDE SAMPLES FROM THE SOUTHERN JUAN DE FUCA RIDGE, NORTH PACIFIC OCEAN

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by

D. L. Sawyer, Jr., G. A. Smyres, J. J. Sjoberg,
and T. G. Carnahan

Bureau of Mines Extractive Metallurgy Technology Program

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	min	minute
cm	centimeter	mL	milliliter
c/min	cycle per minute	mm	millimeter
ft	foot	μm	micrometer
g	gram	oz	troy ounce (31.1 grams)
gal	gallon	pct	weight percent
g/L	gram per liter	psig	pressure, pounds per square inch read directly from gauge
h	hour		
in	inch	STP	standard temperature and pressure (pressure exerted by a column of mercury 760 mm high at 0° C)
m	meter		
mg/L	milligram per liter		

Cl_2-O_2 LEACHING OF MASSIVE SULFIDE SAMPLES FROM THE SOUTHERN JUAN DE FUCA RIDGE, NORTH PACIFIC OCEAN

By D. L. Sawyer, Jr.,[1] G. A. Smyres,[2] J. J. Sjoberg,[3] and T. G. Carnahan[4]

ABSTRACT

Aqueous Cl_2-O_2 leaching procedures developed by the Bureau of Mines to produce zinc chloride from zinc sulfide bulk concentrates were effective in extracting 99 pct of the zinc and 97 pct of the silver contained in samples of massive seafloor sulfides from the southern Juan de Fuca Ridge. Zinc sulfide (sphalerite and wurtzite) mineralization comprised 55 and 88 pct of two specimens provided by the U.S. Geological Survey for this study. Minor occurrences of galena, chalcopyrite, and other minerals in the sulfides permitted the recovery of pregnant liquors that were low in metal values other than zinc, which were successfully purified by a two-step cementation procedure using zinc dust.

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INTRODUCTION

MASSIVE SULFIDE SEAFLOOR ORES

Since 1978, detailed photographic and submersible studies of the oceanic spreading ridge system in the eastern Pacific Ocean have identified polymetallic sulfide deposits and associated submarine hydrothermal springs at the southern Juan de Fuca Ridge west of Oregon (1)[5] (fig. 1). Sulfides on the southern Juan de Fuca Ridge seem to form widespread blanket deposits. The deposits are at a depth of about 2,200 m (7,200 ft), and continued exploration will be required to delineate them and identify their potential commercial value. The U.S. Geological Survey (USGS) made two small samples available to the Bureau of Mines for metallurgical investigations. This report presents the findings of the preliminary investigations.

METALLURGICAL PROCESSING OPTIONS

Several metallurgical processes exist that may be suitable for the recovery of the contained metals. Conventional roasting-leaching-electrowinning (2) is applicable to zinc sulfide concentrates containing 50 to 55 pct zinc and not more than 7 pct iron. Acid-oxygen pressure leaching in a sulfate medium is being practiced at the Cominco smelter in Trail, British Columbia, Canada (3) and produces elemental sulfur rather than sulfuric acid. When pressure leaching is used in conjunction with a smelter, as at Trail, it offers flexibility to the by-product elemental sulfur-H_2SO_4 mix from the smelter. Société Minière et Métallurgique de Pennarroya patented a $CuCl_2$-$NaCl$-HCl leaching method for zinc sulfide concentrate (4). It effectively eliminates iron from the pregnant solutions but makes no provision for separating copper from zinc. The Bureau of Mines has investigated leaching sphalerite concentrates with a strong sulfuric acid system (5) and more complex sulfide concentrates with a novel chlorine-oxygen procedure (6). Chlorine-oxygen leaching rejects iron into the leach residue and produces an iron-free solution for zinc recovery. Because one of the USGS samples contained excessive iron (15 pct), chlorine-oxygen leaching was chosen for the tests.

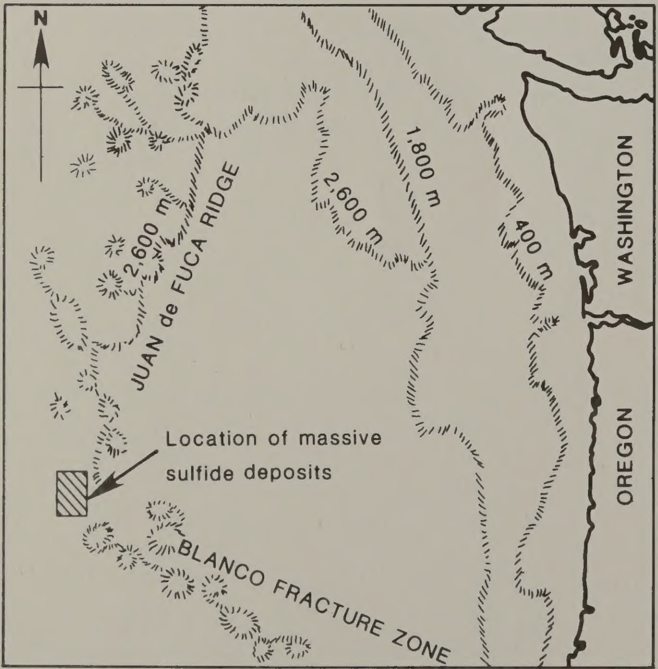

FIGURE 1. - Location of massive sulfide deposits of the southern Juan de Fuca Ridge, North Pacific Ocean.

A simplified process flow diagram for treating zinc concentrates is proposed in figure 2. Zinc dissolves in an aqueous slurry by adding chlorine gas, which forms $ZnCl_2$ and $FeCl_2$ in solution. The reactor is pressurized with oxygen to 50 psig during digestion, and the contents are agitated at 110° C. Iron is precipitated as geothite and releases chloride to complete the zinc leaching. After digestion, the leaching solution contains the $ZnCl_2$, little or no iron, and some impurity metal chlorides. The solution is purified and evaporated to crystallize $ZnCl_2$. The crystals are dried and electrolyzed in a fused-salt cell which produces zinc metal and recycle chlorine.

Two samples of massive sulfides were recovered by dredge sampling from the southern Juan de Fuca Ridge by the USGS (1, 7):

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[5] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

WF-22D-5--Mottled light-gray sulfide, 152 g.

WF-22D-6--Dark-gray sulfide, 147 g.

The analyses of the samples (table 1) suggest that the light-gray sulfide (WF-22D-5) would be satisfactory as a direct feed to an existing roasting-leaching-electrolysis smelter, but that the dark-gray sulfide (WF-22D-6) would be unacceptable because it was too high in iron and too low in zinc. Both samples were subjected to chlorine-oxygen leaching. The smelter-grade sample was tested on the assumption that a chlorine-oxygen leaching plant might treat the ore more economically than a conventional zinc smelter owing to longer shipping distances and high smelter costs.

EXPERIMENTAL WORK

JUAN DE FUCA MASSIVE SULFIDE SAMPLES

Samples WF-22D-5 and WF-22D-6 were supplied as 7- by 8- by 1-cm slabs from larger bulk specimens. Chemical analyses are given in table 1.

Sample Preparation

The USGS bulk sulfide samples were stable in air. Slabs for this study were further washed in distilled water, rinsed in isopropanol, and air-dried at 50° C prior to mineralogy studies. After reference specimens were taken, the

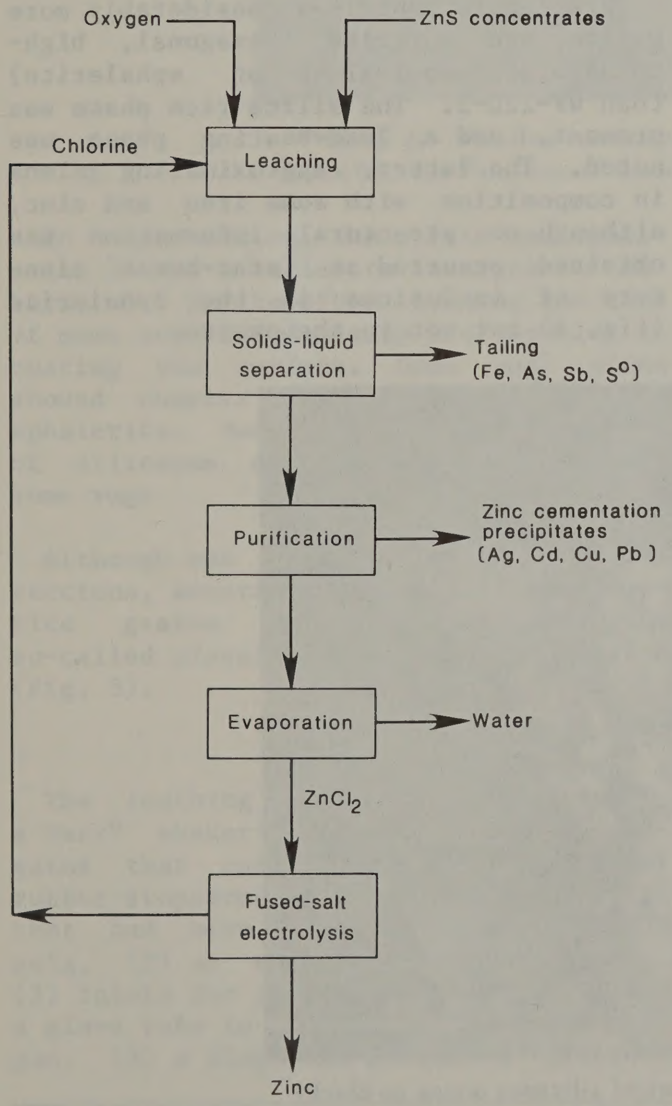

FIGURE 2. - Cl_2-O_2 leaching, molten-salt electrowinning process for zinc sulfide concentrates.

TABLE 1. - Composition of southern Juan de Fuca massive sulfide samples used in this investigation

Component	Sample analysis, pct	
	WF-22D-5	WF-22D-6
Ag	[1]0.024	[2]0.0079
Al_2O_3	.16	.32
As	.038	.048
Au	Trace	Trace
CaO	.01	.12
Cd	.17	.079
Co	.0015	.0029
Cu	.13	.36
Fe	2.9	15
K	<.02	<.02
Li	<.0005	<.0005
MgO	.02	.08
Mn	.0042	.033
Mo	.0060	.0068
Na	.087	.11
Ni	<.0015	<.0015
Pb	.17	.24
S total	30.2	34.4
Sb	.0030	.0056
SiO_2	5.3	6.5
V	.0036	<.0025
Zn	59	37
Total	98.2493	94.3377

[1] 7.1 oz/ton Ag. [2] 2.3 oz/ton Ag.

remainder of the samples were slowly stage-ground to minus 50 mesh with a mortar and pestle to prevent heating, which could form sulfates in air. Powdered samples were slurried in distilled water, filtered, washed with isopropanol, dried at 50° C, and blended to a uniform powder.

Mineralogy

Optical microscopy, scanning electron microscopy, and X-ray microprobe examinations of subsamples of slabs of the two samples, both as received and as polished (cross section), were made to elucidate mineralogy and compositional variation of the minerals identified. The findings were similar to those of Koski (7).

Light-Gray Sulfide (WF-22D-5)

This sample was mainly sphalerite. The iron content of individual sphalerite grains varied from about 5 to 9 pct. The only other phases identified in the polished sections were pyrite and silica (possibly quartz). The pyrite usually contained a small amount of zinc, but occasional grains contained more. It was not possible to obtain exact compositions from the very small grains. The sphalerite sometimes occurred as blocky, fractured grains up to 0.2 mm across; elsewhere it occurred as finely divided material 1 to 2 µm across. The pyrite occurred as small grains of varying shapes in the siliceous material and as rounded inclusions in sphalerite. Open vugs contained intergrown complex euhedral sphalerite crystals, some massive siliceous material, and, in places, spherical siliceous grains. Several small barite "roses" (fig. 3) were noted.

Dark-Gray Sulfide (WF-22D-6)

This sample contained considerably more pyrite and wurtzite (hexagonal, high-temperature equivalent of sphalerite) than WF-22D-5. The silica-rich phase was present, and a lead-bearing phase was noted. The latter, approximating galena in composition with some iron and zinc, although no structural information was obtained, occurred as "star-burst" clusters of inclusions in the sphalerite (fig. 4) but not in the pyrite.

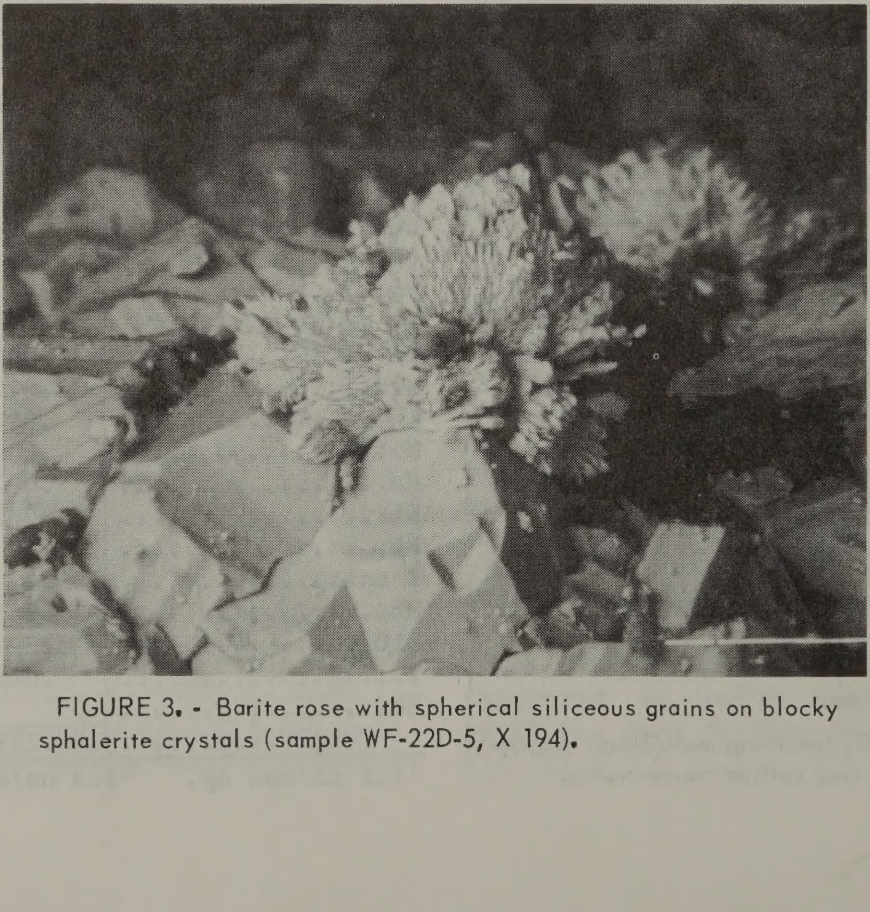

FIGURE 3. - Barite rose with spherical siliceous grains on blocky sphalerite crystals (sample WF-22D-5, X 194).

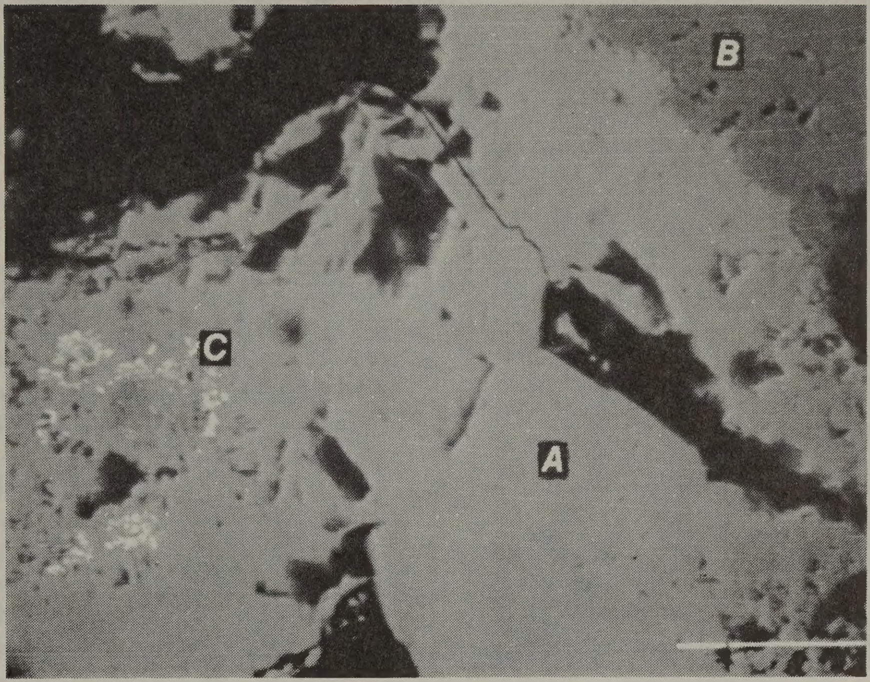

FIGURE 4. - Polished section of dark sulfide showing sphalerite (*A*), pyrite (*B*), and "star burst" lead-bearing (*C*) grains (X 179).

In cross section, the pyrite and sphalerite showed a colloform intergrowth texture, with pyrite often forming the core of some subrounded masses and sphalerite coating the surface. Open vugs often showed complex euhedral crystals of sphalerite. Masses of spherical grains of siliceous material were observed in some vugs.

Although not observed in the polished sections, several clusters of chalcopyrite grains were associated with so-called classic crystals of wurtzite (fig. 5).

PROCEDURE

The leaching tests were conducted in a Parr[6] shaker-type hydrogenation apparatus that consisted of (1) a 500-mL rubber-stoppered glass reaction bottle that had been pressure-tested to 120 psig, (2) an electric heating mantle, (3) inlets for a thermocouple well and a glass tube to admit chlorine and oxygen, (4) a diaphragm-protected pressure gauge, and (5) a rocking mechanism for moving the bottom of the bottle in a 3-in arc at a rate of 225 c/min. Oxygen flow into the glass reactor was measured by a Hastings oxygen flowmeter-totalizer and was recorded as liters of oxygen consumed at standard temperature and pressure conditions (STP). Although the reactions were exothermic, the heat loss from the reactor required that the reactor be heated. A heating mantle with a temperature controller was used. Shaking was continued at the conclusion of each leaching test to permit the slurry to cool slowly.

The glass reactor was charged with the test constituents and was sealed. Agitation was started and chlorine gas was introduced at ambient temperature. Heating was begun, and oxygen overpressure of about 25 psig was used until the reactor was heated to the the 110° C leaching temperature; then the pressure was increased to 50 psig. Since intensive mechanical agitation for dispersal of the oxygen was not available, leaching was carried on for 24 h and with the rocking motion of the reactor. The reactor was cooled and the pH of the slurry was measured. After barium sulfide was added,

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[6] Reference to specific products does not imply endorsement by the Bureau of Mines.

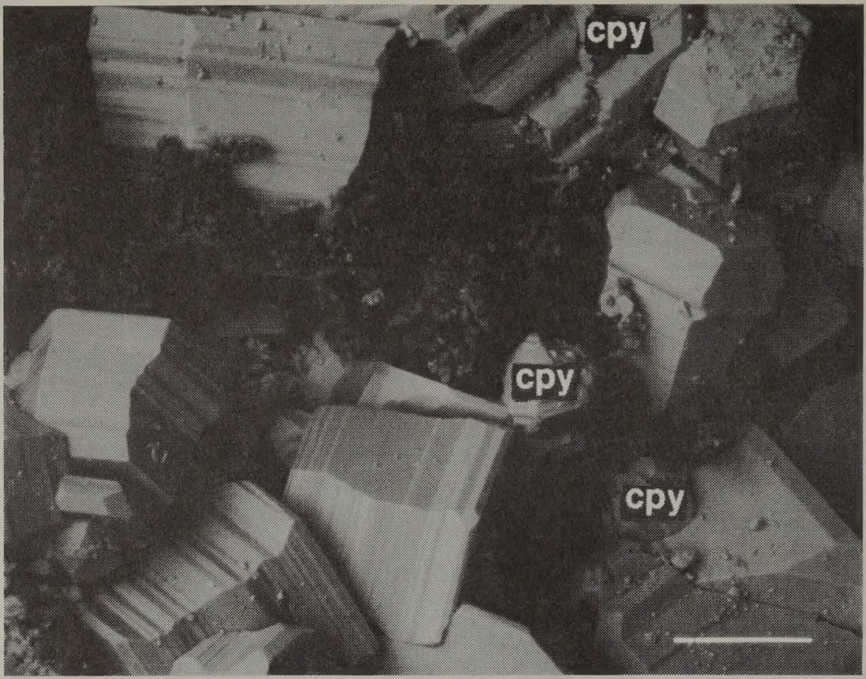

FIGURE 5. - Wurtzite crystals and chalcopyrite (cpy) grains with silicate phase (sample WF-22D-6, X 144).

digestion was continued for an additional 24 h at 110° C and 50 psig O_2. The reactor was cooled, and the final pH was adjusted with concentrated HCl. The slurry was filtered to separate the leached residues from the pregnant solution. Solids were washed with distilled water and air-dried at room temperature. The pregnant liquor, wash water, and dried residue were analyzed.

Filtered pregnant liquors were purified by a two-stage cementation using zinc powder (8). The first-stage addition, at 75° C and with agitation, which used approximately twice the stoichiometric quantity of powdered zinc, was designed to remove all of the Ag, Cu, Pb, Cd, Ni, and Co. The treated solutions were filtered, and about one-fourth of the zinc powder used in the first-stage cementation was added to the 30° C filtrate, which was agitated for 30 min and filtered. Chemical analyses were made on the purified liquors.

RESULTS AND DISCUSSION

The chemical analysis of the ore feed is shown in table 1. An outline of bench-scale procedures and amounts of reagents used is given in table 2, and the leaching results are given in table 3. Chlorine-oxygen leaching extracted more than 99 pct of the zinc and cadmium, 97 pct of the silver, and 78 pct of the copper.

When no previous test data are available on chlorine-oxygen leaching of a sulfide ore, it is not possible to know to what degree side reactions involving oxidation of sulfides to sulfates will occur and the required amount of chlorine for leaching. Since there was material for only one test with each ore sample, the amount of chlorine added was estimated. The result was that too much chlorine was added in each experiment. This produced a pregnant solution containing excess iron because the solution was too acid to permit much of the iron to hydrolyze. In the case of sample WF-22D-6, concentrate was added in three extra stages to consume the excess acid. Each stage included additional leaching

TABLE 2. - Procedural outline for Cl_2-O_2 leaching experiments

Operation and components	Massive sulfide sample	
	WF-22D-5	WF-22D-6
Leaching, g:		
Massive sulfide.....	20.0	32.5
$CaCl_2$ (anhydrous)...	10.0	5.02
H_2O................	80.0	80.0
Cl_2................	12.7	6.2
Total............	122.7	123.72
Leaching agitation and heating..........h..	24	[1]96
pH of leaching slurry, 20° C...............	0.6	1.1
Iron precipitation g:		
BaS.................	2.63	2.0
H_2O................	12.4	10.0
Total............	15.03	12.0
Precipitation agitation and heating..h..	24	24
Acidification:		
HCl (conc).......g..	1.29	NAp
Final pH............	1.0	3.2
2-stage purification, 75° and 30° C:		
Total Zn dust....g..	0.11	0.45
Stirring time..min..	60	60

NAp Not applicable.

[1] 3 small increments of unreacted sulfides were added to the reactor to consume unreacted acidity.

TABLE 3. - Analytical results for Cl_2-O_2 leaching of southern Juan de Fuca massive sulfide samples

Component	Pregnant liquor analyses, before and after Zn cementation, mg/L				Extraction, pct		Leach residue analysis, pct	
	Sample WF-22D-5		Sample WF-22D-6		Sample WF-22D-5	Sample WF-22D-6	Sample WF-22D-5	Sample WF-22D-6
	Before	After	Before	After				
Ag........	100	<2	54	<2	98.7	97.0	0.0020	0.0040
$BaSO_4$.....	ND	ND	ND	ND	ND	ND	24.8	13.2
Ca........	[1]21	ND	710	ND	ND	ND	2.0	2.6
Cd........	250	<2	150	<2	99.4	99.4	.0012	.0005
Cu........	200	<1	810	<1	93.2	78.0	.0120	.13
Fe........	46	40	<.7	<.7	1.0	.0	4.5	23.4
Pb........	38	<6	35	<6	51	53	.0270	.072
S°........	ND	ND	ND	ND	ND	ND	46.9	27.4
S^{2-}.......	ND	ND	ND	ND	ND	ND	.0	2.1
SO_4^{2-}.....	[1]1.1	ND	[1]56	ND	ND	ND	16.3	11.7
Zn........	[1]107	[1]107	[1]109	[1]109	99.7	99.2	.31	.46

ND Not detected. [1] g/L.

at elevated temperature and pressure. Finally, BaS was added to consume the remaining excess acid. Adding BaS was better than adding concentrate because adding too much concentrate would decrease Zn, Ag, and Cu extractions. Sample WF-22D-5 was not treated with additional concentrate but was treated with too much BaS and resulted in a final pH of 4.5. Hydrochloric acid was used to decrease the pH, which insured good copper extraction.

Leaching in the bottle reactor was slow because of poor oxygen-slurry contact. Larger quantities of sphalerite concentrates have been leached by the Bureau in 4 to 6 h with a 50-gal reactor designed specifically for chlorine-oxygen leaching. A similar leaching time is expected for ores represented by the samples tested in this investigation.

The two-stage cementation liquor purification treatment using zinc dust was effective in decreasing base metal impurity concentrations to less than detectable limits (table 3). The relatively low zinc content of the purified liquors (107 and 109 g/L) is undesirable because excessive water must be evaporated to produce zinc chloride crystals for fused-salt electrowinning of zinc metal (9-10). Higher zinc concentration solutions would be produced by recycling part of the pregnant solution to leaching.

SUMMARY AND CONCLUSIONS

A cursory bench-scale investigation of the Cl_2-O_2 leaching of two samples of massive sulfide from the southern Juan de Fuca Ridge, North Pacific Ocean, showed that hydrometallurgical processing of the zinc-rich seafloor deposits is feasible. The extraction of zinc was more than 99 pct. The recovery of silver as a zinc-cementation precipitate was more than 97 pct.

When larger, more representative samples of these deposits become available, additional studies should be undertaken to optimize the process variables and provide information useful in assessing the possible use of the Cl_2-O_2 leaching method for commercial exploitation of the resource.

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